

Unusual Electronic Structure of Few-Layer Grey Arsenic: A Computational Study

Zhen Zhu, Jie Guan, and David Tománek*

Physics and Astronomy Department, Michigan State University, East Lansing, Michigan 48824, USA

(Dated: October 24, 2014)

We use *ab initio* density functional theory to study the equilibrium geometry and electronic structure of few-layer grey arsenic. In contrast to the bulk structure that is semimetallic, few-layer grey As displays a significant band gap that depends sensitively on the number of layers, in-layer strain, layer stacking and inter-layer spacing. A metal-semiconductor transition can be introduced by changing the number of layers or the in-layer strain. We interpret this transition by an abrupt change in the spatial distribution of electronic states near the top of the valence band.

PACS numbers: 73.20.At, 73.61.Cw, 61.46.-w, 73.22.-f

There is growing interest in two-dimensional semiconductors with a significant fundamental band gap and a high carrier mobility. Whereas obtaining a reproducible and robust band gap has turned into an unsurmountable obstacle for graphene [1, 2], the presence of heavy transition metal atoms in layered dichalcogenide compounds limits their carrier mobility[3]. Few-layer structures of layered phosphorus allotropes, such as black phosphorus, are rapidly attracting attention due to their combination of high mobility and significant band gaps [4–6]. We find it conceivable that other isoelectronic systems, such as arsenic, may display similar structural and electronic properties as few-layer phosphorene while being chemically much less reactive [7]. In this respect, the most abundant grey arsenic allotrope is the structural counterpart of the layered A7 or blue phosphorus [5]. Arsenic is commonly known for its toxicity, which is highest for the yellow As allotrope and should not be of concern for few-layer nanostructures. Whereas crystalline grey arsenic displays rhombohedral stacking of layers and is semimetallic [8–14], loss of crystallinity opens a fundamental band gap in the amorphous structure [9, 15]. Even though few-layer grey arsenic has not been studied yet, analogies with blue phosphorene make few-layer arsenic a plausible candidate for a 2D semiconductor.

Here we use *ab initio* density functional theory (DFT) to study the equilibrium geometry and electronic structure of few-layer grey arsenic. This allotrope closely resembles the structure of rhombohedral graphite with the exception of puckering within the honeycomb lattice of the layers. In contrast to the bulk structure that is semimetallic, few-layer grey As displays a substantial band gap that depends sensitively on the number of layers, in-layer strain, layer stacking and inter-layer spacing. A metal-semiconductor transition can be introduced by changing the number of layers or the in-layer strain. We interpret this transition by an abrupt change in the spatial distribution of electronic states near the top of the valence band.

Our computational approach to gain insight into the equilibrium structure, stability and electronic properties of arsenic structures is based on *ab initio* density

functional theory as implemented in the SIESTA [16] and VASP[17] codes. We use periodic boundary conditions throughout the study, with multilayer structures represented by a periodic array of slabs separated by a vacuum region $\gtrsim 15$ Å. Unless specified otherwise, we use the Perdew-Burke-Ernzerhof (PBE) [18] exchange-correlation functional for most calculations. Selected results are compared to the Local Density Approximation (LDA) [19, 20] and other functionals including the OptB86b-vdW functional [21, 22] that provides a better description of van der Waals interactions and the HSE06[23, 24] hybrid functional. In our SIESTA calculations we use norm-conserving Troullier-Martins pseudopotentials [25], and a double- ζ basis including polarization orbitals. The reciprocal space is sampled by a fine grid [26] of $16 \times 16 \times 1$ k -points in the Brillouin zone of the primitive unit cell for 2D structures and $16 \times 16 \times 3$ k -points for the bulk. We use a mesh cutoff energy of 180 Ry to determine the self-consistent charge density, which provides us with a precision in total energy of $\lesssim 2$ meV/atom. All geometries have been optimized using the conjugate gradient method [27], until none of the residual Hellmann-Feynman forces exceeded 10^{-2} eV/Å. Equilibrium structures and energies based on SIESTA have been checked against values based on the VASP code.

In contrast to the AB-stacked isoelectronic black phosphorus, bulk grey arsenic prefers the rhombohedral (or ABC) layer stacking, with the optimized structure shown in Fig. 1. The monolayer of grey As, depicted in top view in Fig. 1(b), resembles the honeycomb lattice of graphene with two atoms per unit cell. Unlike planar graphene, however, the unit cell is puckered, similar to blue (or A7) phosphorus [5], and very different from layered black phosphorus [4]. Interatomic interactions within a monolayer are covalent, resulting in a nearest-neighbor distance of 2.53 Å. The phonon spectrum of a grey arsenic monolayer, displayed in the Supplemental Material [28], shows no soft modes, thus indicating the stability of a free-standing monolayer.

Observed and calculated structural and cohesive properties in grey arsenic are summarized in Table I. The

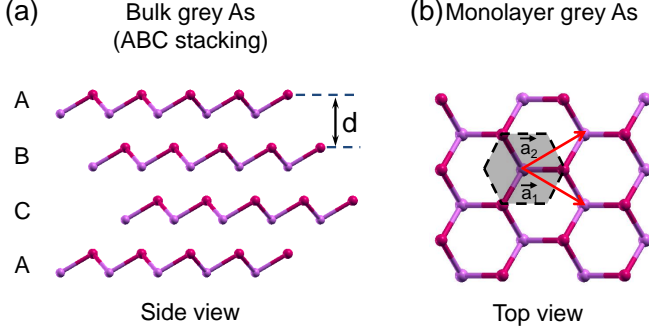


FIG. 1. (Color online) (a) Side view of the rhombohedrally (ABC) stacked layered structure of bulk grey arsenic. (b) Top view of the puckered honeycomb structure of a grey arsenic monolayer. Atoms at the top and bottom of the non-planar layers are distinguished by color and shading and the Wigner-Seitz cell is shown by the shaded region.

calculated inter-layer separation in the ABC-stacked bulk system is $d = 3.58 \text{ \AA}$, similar to the observed value [29]. The interlayer interaction energy of $\approx 0.02 \text{ eV/atom}$, based on PBE, is slightly higher than in blue phosphorus [5]. While this value is likely underestimated, the optB86b value of 0.17 eV/atom and the LDA value of 0.16 eV/atom likely overestimate the interlayer interaction, as discussed in the Supplemental Material [28]. The low interlayer interaction energy, similar to graphite and black phosphorus, suggests that few-layer As may be obtained by mechanical exfoliation from the bulk structure. The small difference in the length of the in-plane lattice vectors $a = |\vec{a}_1| = |\vec{a}_2| = 3.64 \text{ \AA}$ in the isolated monolayer and $a = 3.85 \text{ \AA}$ in the bulk structure is also consistent

TABLE I. Observed and calculated properties of layered grey arsenic. $a = |\vec{a}_1| = |\vec{a}_2|$ is the in-plane lattice constant and d is the interlayer separation, as defined in Fig. 1. E_{coh} is the cohesive energy and E_{il} is the interlayer interaction energy per atom.

| Structure | Bulk(ABC) (expt.) | Bulk(ABC) (theory) | Bulk(AA) (theory) | Monolayer (theory) |
|------------------------|----------------------|-----------------------|----------------------|-----------------------|
| a (Å) | 3.76 ^a | 3.85 ^b | 3.65 ^b | 3.64 ^b |
| | — | 3.85 ^c | 3.64 ^c | 3.61 ^c |
| | — | 3.82 ^d | 3.62 ^d | 3.58 ^d |
| d (Å) | 3.52 ^a | 3.58 ^b | 5.15 ^b | — |
| | — | 3.46 ^c | 4.20 ^c | — |
| | — | 3.47 ^d | 4.31 ^d | — |
| E_{coh} (eV/atom) | 2.96 ^e | 2.86 ^b | 2.85 ^b | 2.84 ^b |
| | — | 3.60 ^c | 3.53 ^c | 3.45 ^c |
| E_{il} (eV/atom) | — | 0.02 ^b | 0.01 ^b | — |
| | — | 0.16 ^c | 0.10 ^c | — |
| | — | 0.17 ^d | 0.13 ^d | — |

^a Experimental data of Ref. [29].

^b Results based on the DFT-PBE functional [18].

^c Results based on the LDA [19].

^d Results based on the optB86b van der Waals functional [21, 22].

^e Experimental data of Ref. [30].

with a weak interlayer interaction. In agreement with the experiment, we find AA-stacked grey arsenic to be less stable than the ABC-stacked structure, even though the energy difference lies within 10 meV/atom . The optimum inter-layer separation in the less favorable AA stacking increases to $d = 5.15 \text{ \AA}$.

In agreement with observations [9], our DFT results indicate that bulk grey arsenic is semimetallic. Our corresponding DFT results for the electronic structure of a monolayer of grey arsenic are presented in Fig. 2. In stark contrast to the bulk, the monolayer structure is semiconducting with an indirect fundamental band gap $E_g \approx 1.71 \text{ eV}$. Comparison with more precise HSE06 [23, 24] hybrid functional calculations, discussed in the Supplemental Material [28], indicates that the PBE value of the band gap is likely underestimated by $\gtrsim 0.4 \text{ eV}$ in few-layer grey arsenic as a common shortcoming of DFT. Still, the electronic structure of the valence and the conduction band region in DFT is believed to closely represent experimental results. Therefore, we expect the charge density associated with frontier orbitals near the top of the valence band, shown in Fig. 2(a), to be represented accurately. These states correspond to the energy range highlighted by the green shading in the band structure plots, which extends from mid-gap to 0.2 eV below the top of the valence band. As seen in the right panel of Fig. 2(a), these frontier orbitals lie in the region of the interatomic bonds and are dominated by in-plane p -orbitals.

As seen in the $E(\vec{k})$ plot in Fig. 2(a), states near the top of the valence band at Γ display a strong dispersion. This is a signature of a very low hole mass, caused by a well connected network of frontier orbitals, which are depicted in the right panel of Fig. 2(a). This is quite different from black phosphorene, where the frontier valence band orbitals are dominated by out-of-plane p -orbitals with little overlap, which reduces the band dispersion and thus increases the hole mass. We find that the effective mass near Γ in few-layer arsenic is not only lower, but – in contrast to black phosphorene [4, 31] – also isotropic. Since high carrier mobility values have been reported in bulk grey arsenic [9], we believe that also few-layer arsenic may display a higher mobility than few-layer black phosphorus.

As seen in Fig. 2(b), a uniform 5% in-layer compression reduces the band gap, but keeps it indirect and does not change drastically the character of the frontier orbitals. According to Fig. 2(d), compression in excess of 10% would close the band gap, turning the monolayer metallic. Interestingly, also a uniform in-layer stretch reduces the band gap in the monolayer significantly. As seen in Fig. 2(c), stretching the monolayer by 5% moves the bottom of the conduction band near Γ . The valence band with an energy eigenvalue -1.3 eV at Γ in the relaxed monolayer, shown in Fig. 2(a), moves up and becomes the top valence band in the stretched layer in Fig. 2(c).

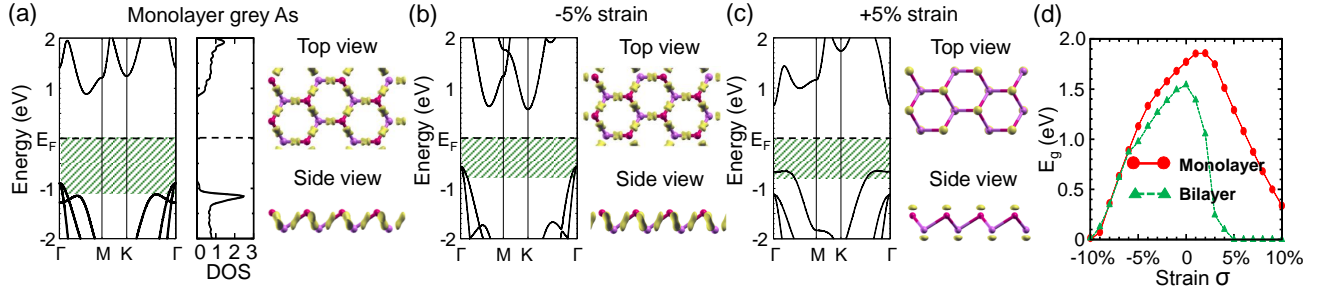


FIG. 2. (Color online) Electronic structure of (a) a relaxed monolayer of grey As, and the same monolayer subject to a uniform in-layer strain of (b) -5% and (c) +5%. The energy range between the Fermi level E_F and 0.2 eV below the top of the valence band is green shaded in the band structure in the left panels. Electron density ρ_{vb} associated with these states, superposed with a ball-and-stick model of the structure, is shown in the right panels. (d) Dependence of the fundamental band gap E_g on the in-layer strain σ in a monolayer and an AB-stacked bilayer of grey As.

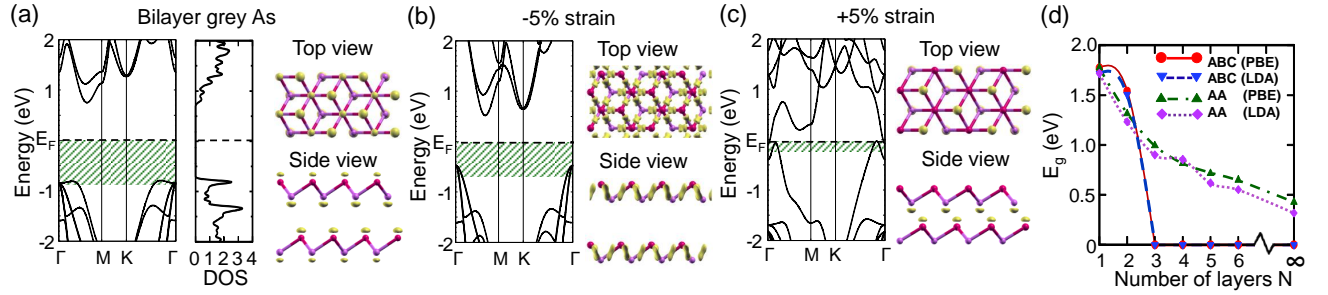


FIG. 3. (Color online) Electronic structure of (a) a relaxed AB-stacked bilayer of grey As, and the same bilayer subject to a uniform in-layer strain of (b) -5% and (c) +5%. The energy range between the Fermi level E_F and 0.2 eV below the top of the valence band is green shaded in the band structure in the left panels. Electron density ρ_{vb} associated with these states, superposed with a ball-and-stick model of the structure, is shown in the right panels. (d) Dependence of the fundamental band gap E_g on the number of layers N and the DFT functional in few-layer As with ABC and AA stacking. The lines in (d) are guides to the eye.

This band gradually flattens near Γ upon stretching, and the monolayer becomes a direct-gap semiconductor at $\sigma \gtrsim +6\%$.

More important is the change in the character of the frontier orbitals caused by the motion of this band relative to the other valence bands near Γ . In contrast to the relaxed and compressed layer depicted in Figs. 2(a) and 2(b), the frontier orbitals in the stretched layer are dominated by p -orbitals normal to the layer. As we will see later, the character change of the frontier orbitals from in-plane to out-of-the-plane has an important effect on the electronic structure of multi-layer systems near E_F . In the simplest example of this difference, shown in Fig. 2(d), which compares a bilayer to a monolayer, the band gap value is essentially the same in both systems during compression, since the frontier orbitals in the layers remain in the plane and do not overlap. The character change of the frontier orbitals to out-of-plane upon stretching is the main cause for the large difference in the band gap value between a monolayer and a bilayer. Quite significant in this respect is our finding that a bilayer should turn metallic for $\sigma \gtrsim 5\%$.

A closer look at the behavior of frontier orbitals in a bilayer subject to different levels of strain is offered in Fig. 3. As seen in Fig. 3(a), the top valence band in the relaxed bilayer has a similar dispersion in the electronic structure near Γ as a stretched monolayer in Fig. 2(c). Also the right panels of the two sub-figures confirm the similar character of the frontier orbitals in a stretched monolayer and a relaxed bilayer. Since the bottom of the conduction band in the relaxed bilayer is not at Γ , this system is an indirect-gap semiconductor with a narrower gap than the relaxed monolayer.

Upon compression, the band ordering near the top of the valence band changes in the bilayer. As seen in Fig. 3(b), the character of the frontier orbitals in a system subject to 5% uniform compression changes to in-plane, similar to a compressed monolayer. A compressed arsenic bilayer remains an indirect-gap semiconductor.

As seen in the right panel of Fig. 3(c), a uniform $\sigma = +5\%$ strain in the bilayer changes the character of the frontier orbitals from in-plane to out-of-plane, similar to our findings for the stretched monolayer reported in Fig. 2(c). The frontier orbitals, which are primarily

distributed in the inter-layer region, bring the two layers closer together. The increased hybridization at a decreased interlayer distance accelerates the band gap closure and, for $\sigma \gtrsim +5\%$, turns the bilayer to a semi-metal.

The overall dependence of the fundamental band gap on the number of layers N and the stacking sequence, depicted in Fig. 3(d), shows a uniform trend of band gap reduction with increasing value of N , which has been noted also for the different layered allotropes of phosphorus [4, 5]. In particular, we find ABC-stacked arsenic slabs with $N > 2$ to be metallic. We also observe notable changes in the optimum inter-layer distance d with changing number of layers and stacking sequence, which strongly affect the electronic structure. We find the optimum inter-layer distance in AA-stacked structures to be much larger than in ABC-stacked structures, which slows down the reduction of the band gap with growing N . To check the validity of this trend, we reproduced the band gap values obtained using both PBE and LDA exchange-correlation functionals for structures optimized by PBE in Fig. 3(d). Small deviations from this trend, associated with the specific functionals, are discussed in the Supplemental Material [28].

The weak inter-layer interaction in layered grey arsenic should allow for a mechanical exfoliation of few layer structures in analogy to graphene and phosphorene. Besides mechanical exfoliation, few-layer grey arsenic has been successfully synthesized by Molecular Beam Epitaxy (MBE), the standard method to grow GaAs, by supplying only As in the growth chamber [32]. Chemical Vapor Deposition (CVD), which had been used successfully in the past to grow graphene[33, 34] and silicene[35], may become ultimately the most common approach to grow few-layer grey arsenic on specific substrates. Substrates such as Ag(111), or even Zr(0001) and Hf(0001) should be advantageous to minimize the lattice mismatch during CVD growth.

From the viewpoint of electronic applications, an ideal 2D semiconductor should combine a sizeable fundamental band gap with a high carrier mobility and chemical stability. Equally important is identifying a suitable way to make electrically transparent contacts. Graphene, with the exception of its vanishing band gap, satisfies the latter three criteria ideally. Transition metal dichalcogenides, including MoS₂, bring the benefit of a nonzero band gap, but display lower intrinsic carrier mobility due to enhanced electron-phonon coupling, primarily caused by the presence of heavy elements such as Mo, and suffer from high tunneling barriers at contacts to the chalcogen atoms. Few-layer systems of black phosphorus and arsenic do show a sizeable band gap, exhibit a higher carrier mobility than MoS₂ [4] and the ability to form transparent contacts to metal leads. Of the two group V elements, the heavier arsenic appears more resilient to oxidation [7]. If indeed few-layer grey arsenic turns out to be chemically stable, it may become an excellent con-

tender for a new generation of nano-electronic devices.

In conclusion, we have used *ab initio* density functional theory to study the equilibrium geometry and electronic structure of few-layer grey arsenic. This allotrope closely resembles the structure of rhombohedral graphite with the exception of puckering within the honeycomb lattice of the layers. In contrast to the bulk structure that is semimetallic, we found that few-layer grey As displays a significant band gap that depends sensitively on the number of layers, in-layer strain, layer stacking and inter-layer spacing. A metal-semiconductor transition can be introduced by changing the number of layers or the in-layer strain. We showed a relationship between this transition and an abrupt change in the spatial distribution of electronic states near the top of the valence band. Due to the weak inter-layer interaction, grey arsenic should exfoliate easily to form few-layer structures. Alternative ways to synthesize few-layer arsenic include MBE and CVD.

We acknowledge useful discussions with Gotthard Seifert and Bilu Liu. Computational resources for this study have been provided by the Michigan State University High Performance Computing Center.

* tomanek@pa.msu.edu

- [1] M. Y. Han, B. Özyilmaz, Y. Zhang, and P. Kim, *Phys. Rev. Lett.* **98**, 206805 (2007).
- [2] D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim, and K. S. Novoselov, *Science* **323**, 610 (2009).
- [3] M. S. Fuhrer and J. Hone, *Nature Nano* **8**, 146 (2013).
- [4] H. Liu, A. T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tomanek, and P. D. Ye, *ACS Nano* **8**, 4033 (2014).
- [5] Z. Zhu and D. Tomanek, *Phys. Rev. Lett.* **112**, 176802 (2014).
- [6] L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, and Y. Zhang, *Nature Nanotech.* **9**, 373 (2014).
- [7] N. Burford, Y.-Y. Carpenter, E. Conrad, and C. D. L. Saunders, “The chemistry of arsenic, antimony and bismuth,” in *Biological Chemistry of Arsenic, Antimony and Bismuth* (John Wiley & Sons, Ltd, 2010) pp. 1–17.
- [8] D. Bullett, *Solid State Commun.* **17**, 965 (1975).
- [9] O. Madelung, *Semiconductors: data handbook*, 3rd ed. (Springer, Berlin, 2004).
- [10] J. H. Xu, E. G. Wang, C. S. Ting, and W. P. Su, *Phys. Rev. B* **48**, 17271 (1993).
- [11] H. Tokailin, T. Takahashi, T. Sagawa, and K. Shindo, *Phys. Rev. B* **30**, 1765 (1984).
- [12] X. Gonze, J.-P. Michenaud, and J.-P. Vigneron, *Phys. Rev. B* **41**, 11827 (1990).
- [13] L. M. Falicov and S. Golin, *Phys. Rev.* **137**, A871 (1965).
- [14] S. Golin, *Phys. Rev.* **140**, A993 (1965).
- [15] M. Kelly and D. Bullett, *Solid State Commun.* **18**, 593 (1976).
- [16] E. Artacho, E. Anglada, O. Dieguez, J. D. Gale, A. Garcia, J. Junquera, R. M. Martin, P. Ordejon, J. M.

- Pruneda, D. Sanchez-Portal, and J. M. Soler, J. Phys. Cond. Mat. **20**, 064208 (2008).
- [17] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
- [18] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- [19] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
- [20] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- [21] J. Klimeš, D. R. Bowler, and A. Michaelides, J. Phys.: Cond. Mat. **22**, 022201 (2010).
- [22] J. Klimeš, D. R. Bowler, and A. Michaelides, Phys. Rev. B **83**, 195131 (2011).
- [23] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
- [24] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, J. Chem. Phys. **125**, 224106 (2006).
- [25] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
- [26] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
- [27] M. R. Hestenes and E. Stiefel, J. Res. Natl. Bur. Stand. **49**, 409 (1952).
- [28] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.000.000000> for details regarding the equilibrium structure, stability, and dependence of electronic structure results on the exchange-correlation functional used in the DFT studies.
- [29] D. Schiferl and C. S. Barrett, J. Appl. Cryst. **2**, 30 (1969).
- [30] C. Kittel, *Introduction to Solid State Physics*, eighth ed. (Wiley, Hoboken, NJ, 2004).
- [31] R. Fei and L. Yang, Nano Lett. **14**, 2884 (2014).
- [32] R. Boča, P. Hajko, L. Benco, I. Benkovský, and D. Faktor, Czechoslovak J. Phys. **43**, 813 (1993).
- [33] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi, and B. H. Hong, Nano Lett. **457**, 706 (2009).
- [34] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, and J. Kong, Nano Lett. **9**, 30 (2009).
- [35] P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet, and G. Le Lay, Phys. Rev. Lett. **108**, 155501 (2012).